PATENT ABSTRACTS OF JAPAN

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(54) METHOD FOR PRODUCING RESIN FINE PARTICLE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for producing resin particles capable of obtaining the resin particles having a high sphericity and uniform particle diameter easily.
SOLUTION: The method for producing resin particles is provided by heating and/or pressurizing a mixture of the resin with a fluid not dissolving the resin at a normal temperature and pressure, and having a process 1 of making at least one component of the liquid state fluid as a supercritical state or semi-supercritical state and a process 2 of lowering the temperature of the liquid state fluid and releasing the pressure.

JAPANESE [JP,2004-143405,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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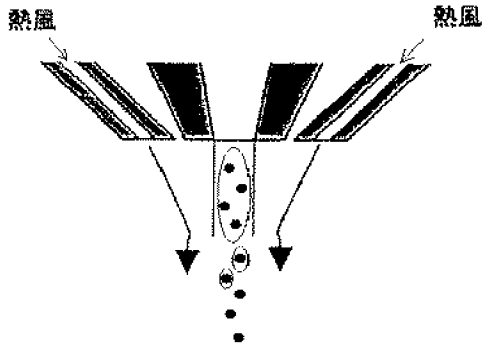
DETAILED DESCRIPTION

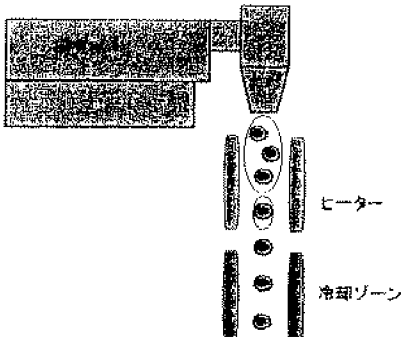
[Detailed Description of the Invention]
[0001]
[Field of the Invention]
Sphericity of this invention is high and it relates to the manufacturing method of the resin particulate which can obtain easily the resin particulate to which particle diameter was equal.
[0002]
[Description of the Prior Art]
A resin particulate begins a slide nature grant agent, a toner, the flatting for paints, and the additive agent for optical diffusion, and is widely used for uses, such as a bulking agent for chromatography, and a carrier for immunodiagnosis reagents. In recent years, the use in IT

Drawing selection Drawing 1

(1)



(2)



[Translation done.]

sectors, such as a spacer for liquid crystal panels and a substrate particle of a conductive particle, is also especially expanded. It is a globular form and the resin particulate used for IT sectors, such as such a spacer for liquid crystal panels and a substrate particle of a conductive particle, etc. is asked for the narrow thing of particle size distribution.

[0003]

Conventionally, the method of grinding physically, using a grinder etc. as a method of producing a resin particulate was used. according to this method -- much resin -- very -- low cost -- and a resin particulate can be obtained easily. However, the shape of the resin particulate obtained in this method was an infinite form, particle diameter was also large, the work of a classification etc. was needed for obtaining the narrow thing of particle size distribution, and the intensity of the resin particulate obtained further also had the problem that there was a tendency which becomes weak.

[0004]

On the other hand, the method of producing a resin particulate with polymerization methods, such as an emulsion polymerization, a distributed polymerization, seed polymerization, and suspension polymerization, is proposed. For example, the method of controlling the particle diameter and particle size distribution of the resin particulate obtained is proposed by producing the monomer dispersion liquid which contain the drop of a desired size beforehand to the patent documents 1, introducing these dispersion liquid into them subsequently to a polymerization tank, and polymerizing under the usual stirring. According to this method, it is a globular form and the narrow resin particulate of particle size distribution can be produced. However, these methods had the problem that it was necessary to adjust polymerization conditions etc. very strictly for producing the resin particulate of the particle diameter made into the purpose in addition to being applicable only to the resin which can polymerize with these polymerization methods.

[0005]

[Patent documents 1]

JP,3-131603,A

[0006]

[Problem(s) to be Solved by the Invention]

In view of the above-mentioned actual condition, sphericity

of this invention is high and an object of this invention is to provide the manufacturing method of the resin particulate which can obtain easily the resin particulate to which particle diameter was equal.
[0007]
[Means for Solving the Problem]
A manufacturing method of a resin particulate this invention is characterized by that comprises the following.
Resin.
The process 1 of heating and/or pressurizing a mixture with a fluid which does not dissolve said resin in ordinary temperature ordinary pressure, and making at least one ingredient of said fluid into a supercritical state or a subcritical state.
The process 2 of lowering and decompressing said fluid.

This invention is explained in full detail below.
[0008]
This invention persons by heating and/or pressurizing wholeheartedly a mixture of resin and a fluid which does not dissolve this resin in ordinary temperature ordinary pressure as a result of examination, using a supercritical state or a subcritical state, lowering at least one ingredient of a fluid after that, and decompressing it, Sphericity finds out that resin particulate suspension in which a resin particulate to which particle diameter was highly equal was suspended in a fluid is obtained, and it came to complete this invention.
A fluid in a supercritical state or a subcritical state has diffusibility which a gas has, and solubility which a fluid has. Therefore, in ordinary temperature ordinary pressure, by using a supercritical state or a subcritical state to resin, even if it is a poor solvent, it becomes a good solvent, and resin can be dissolved and it can distribute. Then, if it lowers the temperature and decompresses, dissolved resin deposits from a fluid serving as a poor solvent again. In a fluid in a supercritical state or a subcritical state, it is thought that resin which deposits is very small and becomes a nearly perfect globular form from resin having suited a very high dispersion state with the surface tension.
[0009]
In this specification, supercritical fluid means a fluid of conditions more than the critical pressure (henceforth Pc), and more than critical temperature (henceforth Tc). A subcritical fluid is in states other than a supercritical state,

and when a pressure of reaction time and temperature are set to P and T, respectively, it means a fluid of conditions of 0.5<P/Pc<1.0 and 0.5<T/Tc or 0.5<P/Pc, and 0.5<T/Tc<1.0. The ranges of a desirable pressure of the above-mentioned subcritical fluid and temperature are 0.6<P/Pc<1.0 and 0.6<T/Tc or 0.6<P/Pc, and 0.6<T/Tc<1.0. However, when a fluid is water, the ranges of temperature used as a subcritical fluid and a pressure are 0.5<P/Pc<1.0 and 0.5<T/Tc or 0.5<P/Pc, and 0.5<T/Tc<1.0. Although temperature expresses Centigrade here, when either Tc or T is minus in Centigrade, a formula showing the above-mentioned subcritical state is not this limitation.

[0010]

In a manufacturing method of a resin particulate of this invention, resin and a fluid which this resin does not melt in ordinary temperature ordinary pressure are mixed first.

It is not limited especially as resin which can apply a manufacturing method of a resin particulate of this invention, For example, Polyester resin [, such as polyethylene terephthalate,];. Polyphenylene-ether-resin;. alicyclic hydrocarbon resin; -- thermoplastic polyimide; -- polyamide-imide-resin; -- polyester imide resin; -- polyolefin resin; -- polystyrene resin; -- polyamide resin; -- polyvinyl-acetal resin; -- polyvinyl-alcohol-resin; -- polyvinyl acetate resin; -- polyvinyl chloride resin. poly (meta-) acrylic ester resin [, such as poly methyl methacrylate,]; -- polyetherimide resin; -- thermoplastic polybenzimidazole resin etc. are mentioned.

For example, an epoxy resin, hardened type modified-polyphenylene-ether resin, Hardened type polyimide resin, silicone resin, benzoxazine resin, melanin resin, Hardening resin, such as a urea resin, allylic resin, phenol resin, unsaturated polyester resin, bismaleimide triazine resin, alkyd resin, furan resin, polyurethane resin, and aniline resin, etc. can be used.

[0011]

It is more desirable to enlarge specific surface area (surface area per unit volume) as shape of the above-mentioned resin in manufacturing a resin particulate in a manufacturing method of a resin particulate of this invention. By enlarging specific surface area, it can be efficient, contact with a fluid and resin can be performed, and processing time can be shortened. By shortening processing time, energy efficiency can be raised and decomposition and degradation of resin

can be controlled. Although not limited especially as a method of enlarging specific surface area, a method of using resin of about 1-5 mm in diameter powder state, a method of using resin beforehand fabricated by the film of 1 mm or less, etc. are mentioned, for example.

[0012]

As the above-mentioned fluid, by ordinary temperature ordinary pressure, especially if the above-mentioned resin is not dissolved, will not be limited, but. It may be a fluid in ordinary temperature ordinary pressure, such as organic media, such as water and alcohol, and it may be a gas in ordinary temperature ordinary pressure, such as carbon dioxide, nitrogen, oxygen, helium, argon, and air, and may be these mixing fluid. However, in ordinary temperature ordinary pressure, it is preferred to contain at least one sort of things which are fluids. When the above-mentioned fluid consists only of what is a gas in ordinary temperature ordinary pressure, in order to dissolve resin into a fluid, very high pressure and temperature may be required.

When using mixing fluid as the above-mentioned fluid, at least one ingredient of a fluid which constitutes mixing fluid should just be in a supercritical state or a subcritical state.

[0013]

As a fluid which is a fluid in the above-mentioned ordinary temperature ordinary pressure, water and/or alcohol are preferred. Since it is cheap, it is economical, and water is a medium which is easy to use, and also is preferred also in respect of influence which it has on environment. Alcohol, such as methanol, is also preferred by same reason. If isopropanol which is the 2nd class alcohol is used, hydrolysis of hydrolytic resin can be controlled.

Unless resin is dissolved by ordinary temperature ordinary pressure, hexane, heptane, Saturation, such as isobutane, isopentane, a neopentane, cyclohexane, and a butene, An unsaturation, a straight chain, branching, cycloalkane; Toluene, benzene, styrene, Aromatic hydrocarbon system organic solvents, such as xylene; Acetone, isobutyl methyl ketone, Ketone system organic solvents, such as isopropyl methyl ketone and methyl ethyl ketone; Isovaleric acid, Carboxylic acid system compounds, such as acetic acid; Diethylether, dibutyl ether, Ether system organic solvents, such as a tetrahydrofuran and dioxane; Ethyl acetate, ester system organic solvent [, such as butyl acetate,]; -- amine system organic solvent [, such as hexamethylenediamine,];

(meta-) -- methyl acrylate. (Meta) Acrylic organic solvents, such as ethyl acrylate; dimethyl sulfoxide, N, and N-dimethylformamide, N, and N-dimethylacetamide, N-methyl-2-pyrrolidone, etc. can be used. As for these organic solvents, the part or all may denaturalize by halogenation etc.

[0014]

The above-mentioned resin and a fluid choose optimal combination in the range by which above-mentioned conditions are fulfilled. For example, when resin is polyethylene terephthalate. As a fluid fluid, methanol is preferred, when resin is poly methyl methacrylate, as a fluid fluid, water is preferred, and when resin is polyolefin resin, as a fluid fluid, mixing fluid of water and alcohol is preferred.

[0015]

In a manufacturing method of a resin particulate of this invention, a mixture of the above-mentioned resin and a fluid is heated and/or pressurized, and the above-mentioned fluid is used as a supercritical state or a subcritical fluid. When the above-mentioned fluid is mixing fluid, at least one ingredient should just become a supercritical state or a subcritical fluid. For example, as for water, it is known with temperature of not less than about 374 **, and a pressure of about 22 or more MPa that methanol will be in a supercritical state with temperature of not less than about 240 ** and a pressure of about 8 or more MPa.

If the above-mentioned mixture is sealed in a resisting pressure container, a supercritical state or a subcritical state can be easily attained by heating. Especially as the above-mentioned heat-resistant container, it cannot be limited, a publicly known thing can be used conventionally, for example, autoclave etc. can be used.

[0016]

A supercritical state or a subcritical state is the environment where activity is very high, since a chemical reaction is promoted dramatically, when resin is left on a supercritical state for a long time, reactions, such as esterification and acetalization, may occur, or a decomposition reaction may occur. Therefore, as for time to put on a supercritical state or a subcritical state, it is preferred to consider it as within a time [which is a grade to which resin does not react / short]. For example, it is preferred to make 250 ** into less than 5 minutes in combination of polyethylene terephthalate

and methanol.

[0017]

It is preferred to stir a mixture of the above-mentioned resin and a fluid in a supercritical state or a subcritical state. ** will be made if the above-mentioned resin makes homogeneity more particle diameter of a resin particulate obtained by being uniformly spread by inside of a fluid by stirring and giving shearing force.

Especially as the method of the above-mentioned stirring, it is not limited but a publicly known method can be used conventionally, For example, a method of using a churning motor for autoclaves, a method of putting stable hard balls (for example, ball made of steel, etc.) in at least 1 resisting-pressure container also in a supercritical state or a subcritical state beforehand, and making a resisting pressure container shake by supercritical state or a subcritical state, etc. are mentioned.

[0018]

After maintaining a predetermined time supercritical state or a subcritical state, it is preferred to lower the above-mentioned fluid promptly and to decompress it. Also into a supercritical state or a subcritical state, resin may react resin as mentioned above for a long time. After predetermined time passes, a reaction of resin can be prevented by quenching with a sealed state and returning to ordinary temperature ordinary pressure. It is not limited especially as a method of quenching, for example, air cooling or a method of water-cooling is mentioned in the above-mentioned resisting pressure container.

Suspension of a resin particulate is obtained by the above process. A resin particulate in obtained suspension is a nearly perfect spherical and thing which also has very narrow particle size distribution.

[0019]

Especially as a method of collecting resin particulates from the above-mentioned resin particulate suspension, it is not limited but a publicly known method can be used conventionally. However, it may be sticky in resin particulate suspension obtained depending on combination of resin and a fluid, and there may be admiration, and when collecting resin particulates, it is necessary to make it resin particulates not coalesce in this case. For example, a method of carrying out heat desiccation in the air using a heat source of a hot wind, far-infrared rays, etc., a method of drying,

once a nonpolar solvent washes, etc. are preferred, dropping the above-mentioned resin particulate suspension. One example of a device which carries out heat desiccation in the air was shown dropping the above-mentioned resin particulate suspension to drawing 1.

[0020]

By heating and/or pressurizing a mixture of resin and a fluid which does not dissolve this resin in ordinary temperature ordinary pressure in a manufacturing method of a resin particulate of this invention, using a supercritical state or a subcritical state, lowering at least one ingredient of a fluid after that, and decompressing it, Suspension of a narrow resin particulate of particle size distribution can be obtained nearly completely spherically. In this invention, controlling only temperature can perform a series of processes by using a sealed resisting pressure container.

If manufacturing conditions are prepared, since a pyrolysis of resin will hardly happen, if resin of the amount of polymers is used as a raw material, a resin particulate of the amount of polymers almost as it is can be obtained. If operation dissolved in a fluid a process until it uses a supercritical state or a subcritical state excluding resin of low molecular weight comparatively is performed even if it is a case where a molecular weight of raw resin has variation, it is the amount of polymers and a narrow resin particulate of molecular weight distribution can also be obtained.

a manufacturing method of a resin particulate of this invention -- getting twisted -- a spherical resin particulate to which particle diameter was very easily [about almost all resin] equal can be obtained.

[0021]

[Example]

Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples.

[0022]

(Example 1)

The methanol 4g and the polyethylene terephthalate 0.2g of about 3 mm in diameter a pellet type were put in and sealed in the resisting pressure container of content volume 10mL. In the heat-resistant container, one ball made from SUS was put beforehand. After vibrating the resisting pressure container and mixing methanol and polyethylene

terephthalate, it heated until it became 250 ** in the oil bath, and methanol was made into the supercritical state. The resisting pressure container was vibrated in this state, and it quenched 5 minutes afterward, and returned to ordinary temperature ordinary pressure.
Thereby, the resin particulate suspension in which the particles of polyethylene terephthalate were suspended in methanol was obtained.
When the resin particulate in the obtained resin particulate suspension was observed, it was nearly completely a globular form and mean particle diameter was 8.6 micrometers. Distribution of the particle diameter of the resin particulate obtained by drawing 2 was shown.
[0023]
(Example 2)
0.2 g of poly methyl methacrylate of the water 4g and about 3 mm in diameter a pellet type was put in and sealed in the resisting pressure container of content volume 10mL. In the thick-proof container, one ball made from SUS was put beforehand. After vibrating the resisting pressure container and mixing water and poly methyl methacrylate, it heated until it became 400 ** all over the sand bath, and water was made into the supercritical state. It quenched 5 minutes afterward and returned to ordinary temperature ordinary pressure.
Thereby, the resin particulate suspension in which the particles of poly methyl methacrylate were suspended underwater was obtained.
[0024]
[Effect of the Invention]
According to this invention, sphericity is high and the manufacturing method of the resin particulate which can obtain easily the resin particulate to which particle diameter was equal can be provided.
[Brief Description of the Drawings]
[Drawing 1]It is a mimetic diagram showing one example of a device which carries out heat desiccation in the air, dropping resin particulate suspension.
[Drawing 2]It is a figure showing distribution of the particle diameter of the resin particulate obtained in Example 1.

[Translation done.]